

# Thermodynamic Study of $\text{UO}_3(\text{g})$ , $\text{UO}_2(\text{OH})_2(\text{g})$ , $\text{UO}_2\text{Cl}_2(\text{g})$ , and $\text{UO}_2\text{F}_2(\text{g})$

*B. B. Ebbinghaus, O. H. Krikorian, D. L. Fleming*

**November 7, 2002**

**U.S. Department of Energy**

Lawrence  
Livermore  
National  
Laboratory

## DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
And its contractors in paper from  
U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
Telephone: (865) 576-8401  
Facsimile: (865) 576-5728  
E-mail: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for the sale to the public from  
U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: (800) 553-6847  
Facsimile: (703) 605-6900  
E-mail: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory  
Technical Information Department's Digital Library  
<http://www.llnl.gov/tid/Library.html>

## Thermodynamic Study of $\text{UO}_3(\text{g})$ , $\text{UO}_2(\text{OH})_2(\text{g})$ , $\text{UO}_2\text{Cl}_2(\text{g})$ , and $\text{UO}_2\text{F}_2(\text{g})$ \*

Bartley B. Ebbinghaus  
Oscar H. Krikorian  
Dennis L. Fleming

Lawrence Livermore National Laboratory

P. O. Box 808

Livermore, CA 94551

Using the transpiration method, the volatility of uranium oxide in the presence of oxygen and water vapor has been measured at temperatures ranging from 1173 to 1573 K and the volatility of uranium oxide in the presence of oxygen and chlorine has been measured at 1175 K. The major vapor species in the presence of oxygen and water vapor are found to be  $\text{UO}_3(\text{g})$  and  $\text{UO}_2(\text{OH})_2(\text{g})$ . Third law treatment of the vaporization data yields  $\Delta H_f^\circ(298)$  values of  $-790.52 \pm 7.32$  and  $-1199.94 \pm 10.25$  kJ/mol, respectively. The major vapor species in the presence of oxygen and chlorine is found to be  $\text{UO}_2\text{Cl}_2(\text{g})$ . Third law treatment of the vaporization data yields a  $\Delta H_f^\circ(298)$  value of  $-1002.04 \pm 3.26$  kJ/mol. From an assessment of all the thermodynamic data available for  $\text{UO}_3(\text{g})$ ,  $\text{UO}_2(\text{OH})_2(\text{g})$ ,  $\text{UO}_2\text{Cl}_2(\text{g})$ , and  $\text{UO}_2\text{F}_2(\text{g})$ , the best  $\Delta H_f^\circ(298)$  values for each of these species are calculated to be  $-796.74 \pm 3.52$ ,  $-1199.94 \pm 10.25$ ,  $-999.64 \pm 2.40$ , and  $-1369.22 \pm 2.87$  kJ/mol, respectively. From these, the  $\Delta H_f^\circ(298)$  values for  $\text{UO}_2\text{ClOH}(\text{g})$ ,  $\text{UO}_2\text{FOH}(\text{g})$ , and  $\text{UO}_2\text{FCl}(\text{g})$  are estimated to be  $-1099.79$ ,  $-1284.58$ , and  $-1184.43$  kJ/mol, respectively. The thermodynamic data for all the vapor species are then applied to conditions one might expect in a thermal oxidation processor for mixed waste to estimate the amount of uranium volatility.

---

\*Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

## Nomenclature

$a(\text{U}_3\text{O}_8)$	Activity of $\text{U}_3\text{O}_8(\text{s})$
$-(G^\circ(T)-H^\circ(298))/T$	Free energy function
$K_1, K_2, \text{ and } K_3$	Equilibrium constants
$p(\text{Cl}_2)$	Partial pressure of $\text{Cl}_2(\text{g})$
$p(\text{H}_2\text{O})$	Partial pressure of $\text{H}_2\text{O}(\text{g})$
$p(\text{O}_2)$	Partial pressure of $\text{O}_2(\text{g})$
$p(\text{UO}_3)$	Partial pressure of $\text{UO}_3(\text{g})$
$p(\text{UO}_2\text{Cl}_2)$	Partial pressure of $\text{UO}_2\text{Cl}_2(\text{g})$
$p(\text{UO}_2(\text{OH})_2)$	Partial pressure of $\text{UO}_2(\text{OH})_2(\text{g})$
$p(\text{U total})$	Total vapor pressure of all uranium vapor species
$\Delta H_f^\circ (298)$	Standard enthalpy of formation at 298 K
$\Delta H_r^\circ (298)$	Standard enthalpy of reaction at 298 K

## 1. Introduction

As part of a study on actinide volatility in incineration and other thermal processes for treatment of mixed waste, the volatility of uranium oxide in the presence of oxygen and water vapor and in the presence of oxygen and chlorine have been measured. Volatility and particle entrainment are the two main sources of possible metal emissions from incinerators and other thermal oxidation processors. A material which volatilizes in a thermal oxidizer will recondense in the offgas preferentially on fine fly ash particulates and as aerosols. These are generally more difficult to capture with air pollution control devices than the larger fly ash particulates. Therefore, the volatility of radioactive materials in thermal processes is very important in assessing the likelihood of radioactive emissions to the atmosphere.

The primary vapor species for uranium are expected to be  $\text{UO}_3(\text{g})$ ,  $\text{UO}_2(\text{OH})_2(\text{g})$ ,  $\text{UO}_2\text{Cl}_2(\text{g})$ ,  $\text{UO}_2\text{F}_2(\text{g})$ ,  $\text{UO}_2\text{ClOH}(\text{g})$ ,  $\text{UO}_2\text{FOH}(\text{g})$ , and  $\text{UO}_2\text{FCl}(\text{g})$ . The vaporization of  $\text{UO}_3(\text{g})$  from  $\text{U}_3\text{O}_8(\text{s})$  in the presence of  $\text{O}_2(\text{g})$  has already been studied by Ackermann, *et al.* [1] and by Dharwadkar, *et al.* [2] using the transpiration method. Additional data are available for  $\text{UO}_3(\text{g})$  from Knudsen effusion measurements involving gaseous equilibria with  $\text{UO}_3(\text{g})$  [4,5]. The vaporization of  $\text{UO}_2(\text{OH})_2(\text{g})$  from  $\text{U}_3\text{O}_8(\text{s})$  in the presence of  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  has been studied by Dharwadkar, *et al.* [2]. The vaporization of  $\text{UO}_2\text{Cl}_2(\text{g})$  from  $\text{U}_3\text{O}_8(\text{s})$  in the presence of  $\text{Cl}_2(\text{g})$  has been studied by Cordfunke and Prins [3], and the vaporization of  $\text{UO}_2\text{F}_2(\text{g})$  from  $\text{UO}_2\text{F}_2(\text{s})$  has been studied by Lau, *et al.* [13], Smirnov and Gorokhov [14], and Knacke, *et al.* [15]. Although the thermodynamics of  $\text{UO}_3(\text{g})$  and  $\text{UO}_2\text{F}_2(\text{g})$  are well known, considerable uncertainty still exists for  $\text{UO}_2(\text{OH})_2(\text{g})$  and  $\text{UO}_2\text{Cl}_2(\text{g})$ . In the experiments by Dharwadkar, *et al.*, the water vapor pressures used were very low. The resulting vapor pressures of  $\text{UO}_2(\text{OH})_2(\text{g})$  are small compared to the  $\text{UO}_3(\text{g})$  vapor pressure. Thus, the vapor pressure of  $\text{UO}_2(\text{OH})_2(\text{g})$  obtained by subtracting the calculated  $\text{UO}_3(\text{g})$  pressure has uncertainties greater than the values being measured. In the experiments by Cordfunke and Prins [3], the oxygen and chlorine pressures were not varied. Thus, the formula for the vaporizing species is still uncertain. No data are available for the mixed vapor species,  $\text{UO}_2\text{ClOH}(\text{g})$ ,  $\text{UO}_2\text{FOH}(\text{g})$ , and  $\text{UO}_2\text{FCl}(\text{g})$ . In this work, the formation of  $\text{UO}_2(\text{OH})_2(\text{g})$

and  $\text{UO}_2\text{Cl}_2(\text{g})$  from  $\text{U}_3\text{O}_8(\text{s})$  in the presence of oxygen and water vapor and oxygen and chlorine, respectively, have been measured. Data for all the uranium vapor species which might be important in thermal oxidation processors for mixed wastes are then assessed.

## 2. Experimental

### 2.1 The Transpiration Method

In the transpiration method [6], a known amount of carrier gas is slowly passed over a sample such that the volatilized material is entrained in the gas flow and is swept out of the chamber and deposited on a collection tube. The amount of material collected can be determined by the weight gain or from quantitative chemical analysis.

The carrier gas may be composed of various reactive gases which will react with the solid material and increase its volatility. In these experiments, the reactive gases are  $\text{O}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ , and  $\text{Cl}_2(\text{g})$ , and the volatilization reactions associated with these species and their equilibrium constants are as follows:

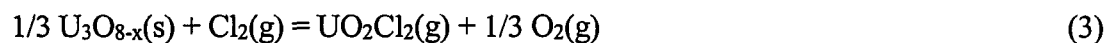


$$K_1 = p(\text{UO}_3)/p(\text{O}_2)^{(1+x)/6} a(\text{U}_3\text{O}_8)^{1/3},$$



$$K_2 = p(\text{UO}_2(\text{OH})_2)/p(\text{O}_2)^{(1+x)/6} p(\text{H}_2\text{O}) a(\text{U}_3\text{O}_8)^{1/3},$$

and



$$K_3 = p(\text{UO}_2\text{Cl}_2)p(\text{O}_2)^{(2-x)/6}/p(\text{Cl}_2)a(\text{U}_3\text{O}_8)^{1/3}.$$

By varying the partial pressures of  $\text{O}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ , and  $\text{Cl}_2(\text{g})$  at a particular temperature, the formula for the vaporizing species can be established.

The non-stoichiometry of uranium oxide at higher temperatures complicates the vaporization equilibria. At relatively modest temperatures, however, the value of  $x$  can be taken to be zero and  $a(\text{U}_3\text{O}_8)$  can be taken to be unity without significant error in the  $\Delta H_f^\circ(298)$  values for  $\text{UO}_3(\text{g})$ ,  $\text{UO}_2(\text{OH})_2(\text{g})$  and  $\text{UO}_2\text{Cl}_2(\text{g})$  calculated from the vaporization data. There have been a

number of studies which have looked at oxygen partial pressure as a function of stoichiometry and temperature for the  $\text{U}_3\text{O}_{8-x}(\text{s})$  phase [18-21]. The error in the calculated  $\Delta H_f^\circ(298)$  values by assuming  $x$  is zero and  $a(\text{U}_3\text{O}_8)$  is unity can be estimated from the free energy of the reaction



at the higher temperatures of measurement. Taking the data of Ackermann and Chang [19] at 1445 K and  $x$  equal to 0.090 which corresponds to the equilibrium composition of uranium oxide in the presence of 1 atm of oxygen, the free energy for the above reaction is given as -0.94 kJ/mol. In analyzing the data herein, most of the data is taken well below 1445 K. Thus, the uncertainty associated with the assumption of  $x$  equal to zero and  $a(\text{U}_3\text{O}_8)$  equal to unity turns out to be considerably less than the uncertainty associated with scatter in the data. For higher temperature data, the treatment herein could result in larger errors.

## 2.2 The Transpiration Apparatuses

Two slightly different transpiration apparatuses were used, one for the oxygen and water vapor experiments and one for the oxygen and chlorine experiments. The unit used for the oxygen and water vapor experiments is illustrated schematically in Figure 1. The apparatus for the oxygen and chlorine experiments is nearly the same except that there is no water bath and a scrubber is used downstream instead of Drierite. In each apparatus, Precision Flow Devices (PFD-401) mass flow controllers were used to control the  $\text{O}_2(\text{g})$ ,  $\text{Ar}(\text{g})$ , and  $\text{Cl}_2(\text{g})$  inputs and to monitor the gas output. In the apparatus for the oxygen and water vapor experiments, the input gases are passed through a water saturator upstream of the furnace and through a Drierite Cartridge ( $\text{CaSO}_4$ ) downstream of the furnace. The water saturator is a 6-mm-thick aluminum vessel with a 800  $\text{cm}^3$  capacity. The partial pressure of water vapor was regulated by controlling the temperature of the water saturator. The water vapor was collected down stream of the furnace in the Drierite Cartridge which was weighed both before and after each experiment to determine the total amount of water vapor transported. In the apparatus for the oxygen and chlorine experiments, the chlorine was collected and immobilized down stream of the furnace in a solution of  $\text{Na}_2\text{S}_2\text{O}_4$  to which a few drops of KI

were added. For both units, the furnace tubes were of alumina and measured 4.5 cm OD by 60 cm long. The input and thermocouple protection tubes were of also alumina, 8 mm OD by about 30 cm long. The outlet or collection tubes were alumina, 8 mm OD by about 30 cm long, or silica glass 6 mm OD by about 30 cm long. The furnaces used were marshall furnaces with Pt/Rh windings and had a uniform temperature hot zone of about 17 cm at around 1000°C. Each end of the furnace tube was sealed off using stainless steel compression fittings with Viton o-ring seals. The input and thermocouple protection tubes pass through compression fittings in the end cap on the up stream side of the furnace, and the collection tube passes through a compression fitting in the end cap on the down stream side of the furnace. The sample boat containing  $\text{U}_3\text{O}_8(\text{s})$  powder rests in the center of the furnace tube. For the oxygen and water vapor experiments, the sample boat was either of platinum or silica glass and measured 2.5 cm wide by 6 cm long by 1 cm high or 3 cm long by 6 cm wide by 0.85 cm high, respectively. For the oxygen and chlorine experiments, the sample boat was of alumina and measured 7.5 cm long by 4.0 cm wide by 0.6 cm high. In both units, just outside of the hot zone both upstream and down stream of the sample boat was placed 6 cm of Kao wool insulation which was held in place on both sides by alumina disks. The temperatures in the hot zone were measured by a type-S thermocouple which was periodically checked against a second thermocouple and showed no difference in readings within  $\pm 2$  K. In both units, all tubing outside of the furnace chamber was stainless steel. For the oxygen and water vapor experiments, the lines leading from the water saturator to the furnace and from the furnace to the Drierite canister were wrapped in heating tape kept at about 160°C to prevent the water vapor from condensing.

### *2.3 Materials and Characterization*

Uranium oxide,  $\text{U}_3\text{O}_8(\text{s})$ , powder formed from depleted U was obtained from the National Institute of Science and Technology (NIST) as a standard reference material and had a stated purity of 99.94%. Oxygen was obtained from Liquid Air. High purity chlorine was obtained from Matheson and argon was obtained from Airco. The water which was used in the water saturators



was distilled and deionized prior to use.

The uranium oxide obtained from NIST was analyzed by X-ray diffraction before use. The sample was found to be primarily  $\text{U}_3\text{O}_8(\text{s})$  with a small amount of a phase tentatively identified as  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ . X-ray analyses after both the oxygen and water vapor experiments and after the oxygen and chlorine experiments showed that the samples were entirely  $\text{U}_3\text{O}_8(\text{s})$ .

#### *2.4 Sample Collection Analyses*

The uranium on the silica and alumina collection tubes was dissolved using 8M  $\text{HNO}_3$  to which a few drops of concentrated HF were added. The tubes were left at least 24 hours in the acid solution to allow for complete dissolution. Repeat tests on the collection tubes showed that less than 2% of the uranium remained in the collection tubes after the first dissolution. The quantity of uranium dissolved was determined by taking a known aliquot of the acid solution and analyzing it by inductively coupled plasma mass spectrometry. This analysis technique was expected to produce analyses accurate within  $\pm 5\%$ .

### **3. Results and Discussion**

#### *3.1 Experimental data*

Experimental transpiration data for the oxygen and water vapor and the oxygen and chlorine experiments are given in Tables 1 and 5, respectively. Most of the oxygen and water vapor experiments were designed such that  $\text{UO}_2(\text{OH})_2(\text{g})$  was present in significant amounts. Data for  $\text{UO}_3(\text{g})$  were obtained such that it could be accounted for in the total volatility of  $\text{U}_3\text{O}_8(\text{s})$  in the presence of oxygen and water vapor. Data for  $\text{UO}_2\text{Cl}_2(\text{g})$  were all taken at 1175 K at varying oxygen and chlorine vapor pressures so that the formula for the vaporizing species could be verified.

In transpiration measurements, it is important to use an appropriate gas flow which is fast enough such that transport by gaseous diffusion is proportionately small but slow enough such that the residence time of the carrier gas is long enough such that equilibrium conditions can be

approximated. In Figure 2, the apparent total vapor pressure of uranium species is plotted as a function of the log of the total gas flow rate in  $\text{cm}^3/\text{min}$  at stp. A plateau region seems to exist from about  $20 \text{ cm}^3/\text{min}$  to at least  $500 \text{ cm}^3/\text{min}$ . Thus, total gas flow rates within this region are expected to yield accurate volatility measurements.

### 3.2 $\text{U}_3\text{O}_8(\text{s})$ volatility induced by $\text{O}_2(\text{g})$

In the presence of oxygen only,  $\text{UO}_3(\text{g})$  is the only vapor species formed in any significant quantity. The data for  $\text{UO}_3(\text{g})$  are treated by the third law method. Free energy functions for  $\text{U}_3\text{O}_8(\text{s})$  were taken from Cordfunke and Konings [11]. Free energy functions for  $\text{O}_2(\text{g})$  were taken from Gurvich, *et al.* [10], and the free energy functions for  $\text{UO}_3(\text{g})$  were taken from Ebbinghaus [7]. Two additional data points for  $\text{UO}_3(\text{g})$  have been added based on extrapolated  $\text{UO}_3(\text{g})$  vapor pressures at 1223 and 1323 K from the experiments with water vapor present. The calculations of these data points are discussed in the following section. The calculated  $\Delta H_f^\circ(298)$  values are summarized in Table 2 which when averaged yield a  $\Delta H_f^\circ(298)$  value of  $401.08 \pm 7.27 \text{ kJ/mol}$ . The data from run numbers 59 and 86 are rejected. Run 59 was a low temperature run at 1173 K where dust carry over or contamination was believed to be a significant fraction of the total amount of uranium collected. Run 86 was rejected because it is one of two runs, 85 and 86, which were analyzed at the same time and yielded suspiciously low uranium values. From the  $\Delta H_f^\circ(298)$  value and the  $\Delta H_f^\circ(298)$  value for  $\text{U}_3\text{O}_8(\text{s})$  given by Cordfunke and Konings [11], a  $\Delta H_f^\circ(298)$  value for  $\text{UO}_3(\text{g})$  was calculated to be  $-790.52 \pm 7.32 \text{ kJ/mol}$ .

### 3.3 $\text{U}_3\text{O}_8(\text{s})$ volatility induced by $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$

In the presence of oxygen and water vapor, both  $\text{UO}_3(\text{g})$  and  $\text{UO}_2(\text{OH})_2(\text{g})$  are present in appreciable quantities. This is apparent by the dependence of the total uranium vapor pressure on the oxygen and water vapor pressures at constant temperature. If both species are present in significant quantities, then the total uranium vapor pressure is given by

$$p(\text{U total}) = K_1 p(\text{O}_2)^{1/6} + K_2 p(\text{O}_2)^{1/6} p(\text{H}_2\text{O}). \quad (5)$$

Dividing out the oxygen contribution yields

$$p(\text{U total})/p(\text{O}_2)^{1/6} = K_1 + K_2 p(\text{H}_2\text{O}). \quad (6)$$

Thus, at any temperature  $p(\text{U total})/p(\text{O}_2)^{1/6}$  should vary linearly with  $p(\text{H}_2\text{O})$ . In Figures 3 and 4,  $p(\text{U total})/p(\text{O}_2)^{1/6}$  is plotted as a function of  $p(\text{H}_2\text{O})$  at 1223 and 1323 K, respectively. At 1223 K, the data fall very close to a straight line with the exception of two data points, runs 85 and 86 which have been rejected. At 1323 K, there is considerable scatter in the data, but the data still seem to fall approximately on a line. Thus, the oxyhydroxide formula of  $\text{UO}_2(\text{OH})_2(\text{g})$  at 1223 K and 1323 K is established with reasonable certainty. After rejecting the data from runs 85 and 86, the data at 1223 and 1323 K where water vapor were present were fit to a straight line and extrapolated to zero water vapor pressure. At 1223 K,  $p(\text{UO}_3)/p(\text{O}_2)^{1/6}$  was calculated to be  $4.451 \times 10^{-9} \text{ atm}^{5/6}$ , and at 1323 K,  $p(\text{UO}_3)/p(\text{O}_2)^{1/6}$  was calculated to be  $5.102 \times 10^{-8} \text{ atm}^{5/6}$ . These values have been included in the third law calculation for  $\text{UO}_3(\text{g})$ .

Taking the  $\Delta H_f^\circ(298)$  value and the free energy functions for  $\text{O}_2(\text{g})$ ,  $\text{U}_3\text{O}_8(\text{s})$ ,  $\text{UO}_3(\text{g})$  given above,  $p(\text{UO}_3)$  was calculated and subtracted from  $p(\text{U total})$  to yield  $p(\text{UO}_2(\text{OH})_2)$  for each data point in which water vapor was present. These calculations are summarized in Table 4. The data for  $\text{UO}_2(\text{OH})_2(\text{g})$  were then treated by the third law method. For some runs  $p(\text{UO}_3)$  was calculated to be greater than  $p(\text{U total})$ . These data had to be rejected. The free energy functions and enthalpies of formation for  $\text{U}_3\text{O}_8(\text{s})$  and  $\text{O}_2(\text{g})$  are the same as those used above, and the free energy functions and enthalpy of formation for  $\text{H}_2\text{O}(\text{g})$  were taken from Gurvich, *et al.* [10]. The calculated  $\Delta H_f^\circ(298)$  values are summarized in Table 4 which when averaged yield a  $\Delta H_f^\circ(298)$  value of  $233.49 \pm 7.12$ . In this analysis, data from runs 16 and 94 have been rejected. In run 16,  $p(\text{UO}_3)$  is almost the same as  $p(\text{U total})$  which results in a  $p(\text{UO}_2(\text{OH})_2)$  which is too small and very uncertain. In run 94, the temperature is so low that all of the uranium carried over is believed to be dust or contamination which yields an artificially high value for  $p(\text{UO}_2(\text{OH})_2)$ . From the  $\Delta H_f^\circ(298)$  value, the  $\Delta H_f^\circ(298)$  value for  $\text{U}_3\text{O}_8(\text{s})$ , and the  $\Delta H_f^\circ(298)$  value for  $\text{H}_2\text{O}(\text{g})$ , the  $\Delta H_f^\circ(298)$  value for  $\text{UO}_2(\text{OH})_2(\text{g})$  was calculated to be  $-1199.94 \pm 10.25 \text{ kJ/mol}$ . The uncertainty has been

calculated by including the standard deviation in the  $\Delta H_f^\circ(298)$  to form  $\text{UO}_3(\text{g})$  as well as the standard deviation in the  $\Delta H_f^\circ(298)$  to form  $\text{UO}_2(\text{OH})_2(\text{g})$ .

### 3.4 $\text{U}_3\text{O}_8(\text{s})$ volatility induced by $\text{O}_2(\text{g})$ and $\text{Cl}_2(\text{g})$

In the presence of oxygen and chlorine, both  $\text{UO}_3(\text{g})$  and  $\text{UO}_2\text{Cl}_2(\text{g})$  are possible vapor species. Therefore, the total uranium pressure is given by

$$p(\text{U total}) = K_1 p(\text{O}_2)^{1/6} + K_3 p(\text{Cl}_2)/p(\text{O}_2)^{1/3} \quad (7)$$

The contribution of  $\text{UO}_3(\text{g})$  turns out to be small. Therefore, it can be neglected. Multiplying by  $p(\text{O}_2)^{1/3}$  yields

$$p(\text{U total})p(\text{O}_2)^{1/3} = K_3 p(\text{Cl}_2) \quad (8)$$

In Figure 5,  $p(\text{U total})p(\text{O}_2)^{1/3}$  has been plotted as a function of  $p(\text{Cl}_2)$ . The data seem to fall along a line which confirms that  $\text{UO}_2\text{Cl}_2(\text{g})$  is the major vapor species. The data where no oxygen was present seem to be low. However, the oxygen in these experiments was assumed to be a third of the total uranium pressure which is the amount expected from eqn (3). It is believed that residual oxygen was present in the furnace tube and Kao wool baffling during the experiment, thus resulting in a higher oxygen pressure than assumed and accounting for the discrepancy in the data. Because of the uncertainty of the oxygen pressures in runs 1 and 8, they have been rejected in the following analysis.

Treating the data from runs 2 through 7 by the third law method, the  $\Delta H_f^\circ(298)$  value was calculated to be  $189.56 \pm 3.15$  kJ/mol and the  $\Delta H_f^\circ(298)$  value was calculated to be  $-1002.04 \pm 3.26$  kJ/mol. The free energy functions and enthalpies of formation for  $\text{U}_3\text{O}_8(\text{s})$ , and  $\text{O}_2(\text{g})$  are the same as given above, and the free energy function for  $\text{Cl}_2(\text{g})$  was taken from Gurvich, *et al.* [10].

## 4. Assessed Standard Enthalpies of Formation

### 4.1 Standard formation enthalpy of $\text{UO}_3(\text{g})$

In addition to this work, Ackermann, *et al.* [1] and Dharwadkar, *et al.* [2] have also determined the vaporization equilibria in which  $\text{UO}_3(\text{g})$  is formed from  $\text{U}_3\text{O}_8(\text{s})$  and  $\text{O}_2(\text{g})$

according to reaction (1). In the work of Ackermann, *et al.*, the volatility of  $\text{U}_3\text{O}_8(\text{s})$  in the presence of  $\text{O}_2(\text{g})$  was measured in the temperature range of 1250 to 1800 K and partial pressures of oxygen either 0.20 or 1.0 atm. In the work of Dharwadkar, *et al.*, the volatility of  $\text{U}_3\text{O}_8(\text{s})$  in the presence of  $\text{O}_2(\text{g})$  was measured in the temperature range of 1525 to 1675 K and a partial pressure of oxygen at 1.0 atm. Treating both sets of data by the third law method using the free energy functions and enthalpies of formation given above yields  $\Delta H_f^\circ(298)$  values of  $393.88 \pm 1.65$  and  $392.74 \pm 0.92$  kJ/mol and  $\Delta H_f^\circ(298)$  values of  $-797.72 \pm 1.85$  and  $-798.86 \pm 1.24$  kJ/mol for the data of Ackermann, *et al.* and Dharwadkar, *et al.*, respectively.

In Figure 6, the log of  $p(\text{UO}_3)/p(\text{O}_2)^{1/6}$  versus  $10^4/T$  is shown for the data points given herein. The solid line is that obtained by a third law treatment of the data. The dashed line is that obtained by averaging the third law treatments of the data of Ackermann, *et al.* and Dharwadkar, *et al.* The data are in good agreement. However, the data of Ackermann, *et al.* and Dharwadkar, *et al.* show considerably less scatter as indicated by the uncertainty in the  $\Delta H_f^\circ(298)$  values. Therefore, in assessing a best value for the  $\Delta H_f^\circ(298)$  value of  $\text{UO}_3(\text{g})$ , the  $\Delta H_f^\circ(298)$  values for  $\text{UO}_3(\text{g})$  obtained from the data of Ackermann, *et al.* and Dharwadkar, *et al.* were weighted double and averaged with the value obtained from the data herein to yield a best  $\Delta H_f^\circ(298)$  value of  $-796.74 \pm 3.52$  kJ/mol.

#### 4.2 Standard formation enthalpy of $\text{UO}_2(\text{OH})_2(\text{g})$

Dharwadkar, *et al.* [2] have also determined the equilibria in which  $\text{UO}_2(\text{OH})_2(\text{g})$  is formed from  $\text{U}_3\text{O}_8(\text{s})$ ,  $\text{O}_2(\text{g})$ , and  $\text{H}_2\text{O}(\text{g})$  according to reaction (2). In the work of Dharwadkar, *et al.*, the volatility of  $\text{U}_3\text{O}_8(\text{s})$  in the presence of  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  was measured in the temperature range of 1320 to 1625 K and partial pressures of oxygen and water vapor ranging from 0.80 to 0.97 atm and 0.20 to 0.03 atm, respectively. Treating the data by the third law method using the free energy functions and enthalpies of formation given above yields a  $\Delta H_f^\circ(298)$  value of  $154.13 \pm 6.19$  kJ/mol and a  $\Delta H_f^\circ(298)$  value of  $-1279.30 \pm 6.25$  kJ/mol.

In Figure 7, the log of  $p(\text{UO}_2(\text{OH})_2)/p(\text{O}_2)^{1/6}p(\text{H}_2\text{O})$  versus  $10^4/T$  is shown for the data points given herein. The solid line is that obtained by a third law treatment of the data. The dashed

line is that obtained by a third law treatment of the data of Dharwadkar, *et al.*, which disagrees considerably from the data herein. It is difficult to understand why such a large discrepancy exists. Dharwadkar, *et al.* used very low vapor pressures of water, never greater than 0.20 atm. In many cases, the pressures of  $\text{UO}_2(\text{OH})_2(\text{g})$  were therefore small in comparison to the pressures of  $\text{UO}_3(\text{g})$ . Therefore,  $p(\text{UO}_2(\text{OH})_2)$  was uncertain. In their analyses, Dharwadkar, *et al.* also used a colorimetric technique [12] to determine the uranium content in their collection tubes. In this method, there are a number of interfering ions which may have present and altered their analyses. Although the discrepancy remains unexplained, the values given herein are taken to be closer to the true values. Therefore, the best assessed  $\Delta H_f^\circ(298)$  value for  $\text{UO}_2(\text{OH})_2(\text{g})$  is  $-1199.94 \pm 10.25$  kJ/mol.

#### 4.3 Standard formation enthalpy of $\text{UO}_2\text{Cl}_2(\text{g})$

Cordfunke and Prins [3] have also determined the vaporization equilibria in which  $\text{UO}_2\text{Cl}_2(\text{g})$  is formed from  $\text{U}_3\text{O}_8(\text{s})$  and  $\text{Cl}_2(\text{g})$  by reaction (3). In the work of Cordfunke and Prins, the volatility of  $\text{U}_3\text{O}_8(\text{s})$  in the presence of  $\text{Cl}_2(\text{g})$  was measured in the temperature range of 1135 to 1330 K and a chlorine pressure near 1.0 atm. Treating the data by the third law method using the free energy functions and enthalpies of formation given above yields a  $\Delta H_f^\circ(298)$  value of  $194.37 \pm 1.24$  kJ/mol and a  $\Delta H_f^\circ(298)$  value of  $-997.23 \pm 1.49$  kJ/mol.

In Figure 8, the log of  $p(\text{UO}_2\text{Cl}_2)p(\text{O}_2)^{1/3}/p(\text{Cl}_2)$  versus  $10^4/T$  is shown for the data points given herein. The solid line is that obtained from a third law fit of the data. The dashed line is that obtained from a third law treatment of the data of Cordfunke and Prins. The best  $\Delta H_f^\circ(298)$  value was obtained by averaging the value obtained herein with that obtained from the data of Cordfunke and Prins to yield  $-999.64 \pm 2.40$  kJ/mol.

#### 4.4 Standard enthalpy of $\text{UO}_2\text{F}_2(\text{g})$

The sublimation reaction of



has been studied by Lau, *et al.* [13], Smirnov and Gorokhov [14], and Knacke, *et al.* [15]. These data have all been reanalysed here using the data of Ebbinghaus [7] for the free energy functions of  $\text{UO}_2\text{F}_2(\text{g})$ . The free energy functions for  $\text{UO}_2\text{F}_2(\text{s})$  have been calculated from enthalpy increment measurements on  $\text{UO}_2\text{F}_2(\text{s})$  given by Cordfunke, *et al.* [16] and the  $S^\circ(298)$  and  $\Delta H_f^\circ(298)$  values of  $135.56 \pm 0.42$  J/mol-K and  $-1635.5 \pm 1.3$  kJ/mol given by Grenthe, *et al.* [17]. The free energy function for  $\text{UO}_2\text{F}_2(\text{s})$  was fit to the equation

$$-(G^\circ - H^\circ(298))/T = 163.588 - 252.753(T/1000) + 689.437 (T/1000)^2 - 584.267(T/1000)^3 + 177.360(T/1000)^4 \quad (10)$$

over the temperature range of 298 to 1200 K. Treating the data of Lau, *et al.* [13], Smirnov and Gorokhov [14], and Knacke, *et al.* [15] by the third law method yields  $\Delta H_f^\circ(298)$  values of  $285.20 \pm 0.26$ ,  $285.89 \pm 1.06$ , and  $279.18 \pm 5.25$  kJ/mol, respectively. In treating Smirnov and Gorokhov's data, the data points taken at temperatures of 1028 and 1036 K were rejected because they deviated dramatically from the other points which showed a very small deviation. No data points were rejected in the other third law treatments. Using the  $\Delta H_f^\circ(298)$  value for  $\text{UO}_2\text{F}_2(\text{s})$ , the  $\Delta H_f^\circ(298)$  value for  $\text{UO}_2\text{F}_2(\text{g})$  was calculated to be  $-1368.29 \pm 1.32$ ,  $-1367.61 \pm 1.67$ , and  $-1374.32 \pm 5.40$  kJ/mol for the data of Lau, *et al.* [13], Smirnov and Gorokhov [14], and Knacke, *et al.* [15], respectively. Since the statistical uncertainty is considerably greater in the data of Knacke, *et al.*, it was weighed half when averaged with the other values in order to obtain the recommended  $\Delta H_f^\circ(298)$  value of  $-1369.22 \pm 2.87$  kJ/mol for  $\text{UO}_2\text{F}_2(\text{g})$ .

#### 4.5 Mixed species: $\text{UO}_2\text{ClOH}(\text{g})$ , $\text{UO}_2\text{FOH}(\text{g})$ , and $\text{UO}_2\text{FCl}(\text{g})$

Since no data are available for these species, the  $\Delta H_f^\circ(298)$  values were taken to be an average of the  $\Delta H_f^\circ(298)$  values for the constituent species. For example, the  $\Delta H_f^\circ(298)$  value for  $\text{UO}_2\text{ClOH}(\text{g})$  was taken to be an average of the  $\Delta H_f^\circ(298)$  value for  $\text{UO}_2\text{Cl}_2(\text{g})$  and  $\text{UO}_2(\text{OH})_2(\text{g})$ . In this manner, the  $\Delta H_f^\circ(298)$  values for  $\text{UO}_2\text{ClOH}(\text{g})$ ,  $\text{UO}_2\text{FOH}(\text{g})$ , and  $\text{UO}_2\text{FCl}(\text{g})$  were estimated to be  $-1099.79$ ,  $-1284.58$ , and  $-1184.43$  kJ/mol, respectively. The free energy functions for these species can be estimated from their constituent species according to the method given previously

[7].

All of the assessed  $\Delta H_f^\circ(298)$  values for the uranium vapor species are summarized in Table

7.

## 5. Application to Thermal Oxidation Processes

The thermodynamic data for the uranium vapor species are now applied to a thermal oxidation processor. Typically this would be an incinerator but may include other processors as well. As a worst case, uranium can be taken to be present as  $U_3O_8(s)$  in the thermal oxidation processor. In other words, the activity of  $U_3O_8(s)$  is taken to be unity. If  $U_3O_8(s)$  reacts with the residual ash to form a mixed oxide, then its activity and hence its volatility may be reduced. The partial pressures of  $O_2(g)$  and  $H_2O(g)$  will vary a small amount and the partial pressures of  $HCl(g)$  and  $HF(g)$  will vary considerably depending upon the waste feed composition, the amount of excess air supplied, and in some cases the medium of oxidation. For these calculations, the partial pressures of  $O_2(g)$  and  $H_2O(g)$  are each taken to be 0.10 atm and the partial pressures of  $HCl(g)$  and  $HF(g)$  are each taken at compositions of 0.001 and 0.10 atm. In Figure 9, the partial pressures of the various uranium vapor species as a function of temperature are shown for a condition with high, 0.10 atm, and low, 0.001 atm,  $HCl(g)$  pressure. In Figure 10, the partial pressures of the various uranium vapor species as a function of temperature are shown for a condition with high  $HF(g)$  pressure, 0.10 atm, and low  $HF(g)$ , 0.001 atm, pressure. The  $UO_2Cl_2(g)$  and  $UO_2F_2(g)$  species dominate at the lower temperatures. In both Figures 9 and 10 the plutonium vapor species are shown for comparison. Data for the plutonium species are taken from Ebbinghaus [7] and Krikorian, *et al.* [22] Generally, the plutonium vapor species are present at much lower concentrations than the uranium vapor species.

A typical afterburner on an incinerator may operate around 1400 K. At this temperature, the total pressure of uranium vapor species assuming uranium present as  $U_3O_8(s)$ ,  $O_2(g)$  and  $H_2O(g)$  vapor pressures of 0.10 atm each, and  $HCl(g)$  and  $HF(g)$  pressures of 0.01 and 0.002 atm, respectively, is calculated to be  $8.21 \times 10^{-7}$  atm. The breakdown of the various species would be



46.38%  $\text{UO}_3(\text{g})$ , 2.05%  $\text{UO}_2(\text{OH})_2(\text{g})$ , 24.79%  $\text{UO}_2\text{Cl}_2(\text{g})$ , 0.83%  $\text{UO}_2\text{F}_2(\text{g})$ , 14.26%  $\text{UO}_2\text{ClOH}(\text{g})$ , 2.61%  $\text{UO}_2\text{FOH}(\text{g})$ , and 9.08%  $\text{UO}_2\text{FCl}(\text{g})$ . If the output gas flow is 40 kmol/h (about 580 SCFM), then the rate of uranium volatilization would be 7.82 g/h. This is a significant amount of uranium which is volatilized. However, most of this material would collect on the walls of the processor and in the offgas filtration devices rather than be released to the atmosphere.

## 6. Conclusions

From the volatility of  $\text{U}_3\text{O}_8(\text{s})$  in the presence of oxygen and water vapor and in the presence of oxygen and chlorine, the thermodynamics of  $\text{UO}_3(\text{g})$ ,  $\text{UO}_2(\text{OH})_2(\text{g})$ , and  $\text{UO}_2\text{Cl}_2(\text{g})$  have been determined. These data are assessed along with other available data in the literature to provide  $\Delta H_f^\circ(298)$  values for  $\text{UO}_3(\text{g})$ ,  $\text{UO}_2(\text{OH})_2(\text{g})$ ,  $\text{UO}_2\text{Cl}_2(\text{g})$ , and  $\text{UO}_2\text{F}_2(\text{g})$ , and estimated  $\Delta H_f^\circ(298)$  values for  $\text{UO}_2\text{ClOH}(\text{g})$ ,  $\text{UO}_2\text{FOH}(\text{g})$ , and  $\text{UO}_2\text{FCl}(\text{g})$ .

Application to thermal oxidation processors shows that all these species can be important.  $\text{UO}_2\text{Cl}_2(\text{g})$  and  $\text{UO}_2\text{F}_2(\text{g})$  tend to be most important relative to the other uranium vapor species at the lower temperatures.  $\text{UO}_2(\text{OH})_2(\text{g})$  tends to be most important at the intermediate temperatures, and  $\text{UO}_3(\text{g})$  tends to be most important at the higher temperatures. The mixed species,  $\text{UO}_2\text{ClOH}(\text{g})$ ,  $\text{UO}_2\text{FOH}(\text{g})$ , and  $\text{UO}_2\text{FCl}(\text{g})$ , are most important when their constituent species are present in about equal concentrations.

## References

- [1] R. J. Ackermann, R. J. Thorn, C. Alexander, M. Tetenbaum, *J. Phys. Chem.*, **64** (1960) 350.
- [2] S. R. Dharwadkar, S. N. Tripathi, M. D. Karkhanavala, M. S. Chandrasekharaiah, *Proc. Thermodynamics of Nuclear Materials*, Vienna, Austria, Oct. 21-25, 1974 (IAEA, 1975).
- [3] E. H. P. Cordfunke and G. Prins, *J. Inorg. Nucl. Chem.*, **36** (1974) 1291.
- [4] G. DeMaria, R. P. Burns, J. Drowart, and M. G. Inghram, *J. Chem. Phys.*, **32** (1960) 1373.
- [5] C. Younes, L. D. Nguyen, and A. Pattoret, *High Temp.-High Press.*, **13** (1981) 105.
- [6] F. D. Richardson and C. B. Alcock, "Chemical Equilibria," in *Physiochemical Measurements at High Temperatures*, edited by J. O'M. Bockris, J. L. White, and J. D. Mackenzie, Butterworths Sci. Publ., London, 1959, pp 135-170.
- [7] B. B. Ebbinghaus, Lawrence Livermore National Laboratory report, UCRL-JC-122278 (1994).
- [8] O. H. Krikorian, *High Temp.-High Press.*, **14** (1982) 387-397.
- [9] D. W. Green, *Int. J. Thermophys.*, **1** (1980) 61-71.
- [10] L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4<sup>th</sup> ed, Vol.1 (Hemisphere Publ., New York, 1989).
- [11] E. H. P. Cordfunke and R. J. M. Konings, eds., *Thermochemical Data for Reactor Materials and Fission Products* (Elsevier, North-Holland, 1990).
- [12] J. H. Yoe, F. Will, III, and R. A. Black, *Analy. Chem.*, **25** (1953) 1200-1204.
- [13] K. H. Lau, R. D. Brittain, and D. L. Hidebrand, *J. Phys. Chem.*, **89** (1985) 4369-4373.
- [14] V. K. Smirnov and L. N. Gorokhov, *Russ. J. Phys. Chem.*, **58** (1984) 346-349.
- [15] V. O. Knacke, G. Lossmann, and F. Muller, *Z. Anorg. Allg. Chem.*, **371** (1969) 32-37.
- [16] E. H. P. Cordfunke, R. P. Muis, and G. Prins, *J. Chem. Thermo.*, **11** (1979) 819-823.
- [11] H. Wanner and I. Forest, eds., *Chemical Thermodynamics of Uranium* (Elsevier, North-Holland, 1992).
- [18] P. S. Murti, R. B. Yadav, H. P. Nawada, P. R. Vasudeva Rao, and C. K. Mathews, *Thermochimica Acta*, **140** (1989) 299-303.

- [19] R. J. Ackermann and A. T. Chang, *J. Chem. Thermo.*, **5** (1973) 873-890.
- [20] A. Caneiro and J. P. Abriata, *J. Nucl. Mater.*, **126** (1984) 255-267.
- [21] T. Fujino, H. Tagawa, and T. Adachi, *J. Nucl. Mater.*, **97** (1981) 93-103.
- [22] O. H. Krikorian, A. S. Fontes, Jr., B. B. Ebbinghaus, and M. G. Adamson, *J. Nucl. Mater.*, **247** ((1997) 161-171.

Table 1. Summary of transpiration experiments on uranium oxide in the presence of oxygen and water vapor.

run #	T (K)	time (min)	moles total	p(O <sub>2</sub> ) (atm)	p(H <sub>2</sub> O) (atm)	p(U total) (atm)
7	1323	180	0.8739	0.4594	0.5406	9.278x10 <sup>-8</sup>
8	1323	180	0.4267	0.4706	0.5294	9.481x10 <sup>-8</sup>
9	1323	180	0.3564	0.3381	0.6619	1.122x10 <sup>-7</sup>
10	1323	180	0.2008	0.4505		6.815x10 <sup>-8</sup>
11	1323	180	0.3929	0.1227	0.8773	1.326x10 <sup>-7</sup>
12	1323	180	0.4457	0.4546		2.882x10 <sup>-8</sup>
13	1473	180	0.4778		0.5797	6.190x10 <sup>-7</sup>
14	1323	180	0.6937	0.2245	0.2245	6.556x10 <sup>-8</sup>
15	1223	1200	2.9713	0.5496		2.177x10 <sup>-9</sup>
16	1323	180	0.4339	0.4628	0.5372	4.667x10 <sup>-8</sup>
17	1473	120	0.6102	0.4387	0.5613	1.727x10 <sup>-6</sup>
18	1323	120	0.1864	0.2586	0.7414	1.546x10 <sup>-7</sup>
19	1323	180	0.4417	0.4546		2.825x10 <sup>-8</sup>
20	1373	120	1.1854	0.4517	0.5483	2.566x10 <sup>-7</sup>
21	1223	1440	3.3966	0.5769	0.4231	2.297x10 <sup>-9</sup>
22	1373	180	0.1575	0.5098	0.4902	2.774x10 <sup>-7</sup>
23	1373	240	0.0748*	0.4291	0.5709	1.213x10 <sup>-7</sup>
24	1373	180	0.5634*	0.4276	0.5724	2.194x10 <sup>-7</sup>
25	1373	120	3.8131	0.4212	0.5788	2.016x10 <sup>-7</sup>
26	1323	180	0.6524	0.6154	0.3846	5.815x10 <sup>-8</sup>
27	1323	180	0.4853	0.8273	0.1727	4.501x10 <sup>-8</sup>
31	1573	60	0.7625	0.4212	0.5788	1.091x10 <sup>-5</sup>
32	1573	60	2.1186	0.1516	0.8484	6.246x10 <sup>-6</sup>
33	1573	180	0.7129	0.5632	0.4368	1.226x10 <sup>-5</sup>
34	1573	180	0.4015	1.000		2.595x10 <sup>-5</sup>
46	1373	540	1.2046	1.000		4.858x10 <sup>-8</sup>
47	1373	120	2.5573	0.4187	0.5813	2.673x10 <sup>-7</sup>
49	1473	240	0.3212	1.000		2.354x10 <sup>-6</sup>
50	1273	480	0.6425	1.000		1.975x10 <sup>-8</sup>
55	1173	1950	5.2302	0.4159	0.5841	1.912x10 <sup>-9</sup>
56	1373	480	0.2978	0.4315	0.5685	4.274x10 <sup>-7</sup>
57	1373	>180	>.5419	>0.2964	<0.7036	<1.775x10 <sup>-7</sup>
58	1373	440	0.9371	0.4190	0.5810	3.022x10 <sup>-7</sup>
59	1173	540	0.6023	1.000		9.137x10 <sup>-9</sup>
60	1373	510	2.6364	0.4315	0.5685	2.358x10 <sup>-7</sup>
76	1273	440	1.3620	0.3026	0.6974	1.761x10 <sup>-8</sup>
78	1323	480	1.2013	0.8022	0.1978	3.242x10 <sup>-8</sup>
79	1223	1890	5.5931	0.3166	0.6834	7.939x10 <sup>-9</sup>
85	1223	1810	3.5596	0.7940	0.2060	8.025x10 <sup>-10</sup>
86	1223	1890	3.3729	1.000		4.110x10 <sup>-10</sup>
88	1323	515	2.9592	0.1398	0.8602	5.655x10 <sup>-8</sup>
90	1323	475	1.4686	0.3030	0.6970	6.848x10 <sup>-8</sup>
91	1223	1680	6.8700	0.1637	0.8363	8.451x10 <sup>-9</sup>
94	826	5785	12.5079	0.4127	0.5873	2.687x10 <sup>-11</sup>

\* moles of water vapor calculated from water saturator temperature

Table 2. Third law treatment for the reaction  $1/3 \text{ U}_3\text{O}_8(\text{s}) + 1/6 \text{ O}_2(\text{g}) = \text{UO}_3(\text{g})$ .

run #	T (K)	$K_{\text{eq}}$	$-\Delta G^\circ$ (kJ/mol)	$-(\Delta G^\circ - \Delta H^\circ(298))/T$ (J/mol-K)	$\Delta H^\circ(298)$ (kJ/mol)
10	1323	$7.784 \times 10^{-8}$	-180.08	163.443	396.35
12	1323	$3.286 \times 10^{-8}$	-189.57	163.443	405.80
15	1223	$2.406 \times 10^{-9}$	-201.83	164.951	403.60
19	1323	$3.221 \times 10^{-8}$	-189.79	163.443	406.06
34	1573	$2.595 \times 10^{-5}$	-138.12	159.961	389.77
46	1373	$4.858 \times 10^{-8}$	-192.27	162.716	415.71
49	1473	$2.354 \times 10^{-6}$	-158.74	161.310	396.38
50	1273	$1.975 \times 10^{-8}$	-187.80	164.187	396.84
59	1173	$9.137 \times 10^{-9}$	-180.57	165.734	375.01
	rejected				
86	1223	$4.110 \times 10^{-10}$	-219.80	164.951	421.57
	rejected				
*	1323	$5.102 \times 10^{-8}$	-186.71	163.443	402.98
*	1223	$4.451 \times 10^{-9}$	-195.58	164.951	<u>397.35</u>
					$401.08 \pm 7.27$
		$\Delta H_f^\circ(298)$ (kJ/mol)			
$\text{U}_3\text{O}_8(\text{s})$		$-3574.80 \pm 2.50$			
$\text{UO}_3(\text{g})$		$-790.52 \pm 7.32$			

Table 3. Calculation of  $p(\text{UO}_2(\text{OH})_2)$  by subtracting  $p(\text{UO}_3)$  from  $p(\text{U total})$ .

run #	T (K)	$p(\text{U total})$ (atm)	$p(\text{UO}_3)$ (atm)	$p(\text{UO}_2(\text{OH})_2)$ (atm)
7	1323	$9.2779 \times 10^{-8}$	$4.4300 \times 10^{-8}$	$4.8479 \times 10^{-8}$
8	1323	$9.4811 \times 10^{-8}$	$4.4478 \times 10^{-8}$	$5.0333 \times 10^{-8}$
9	1323	$1.1222 \times 10^{-7}$	$4.2093 \times 10^{-8}$	$7.0127 \times 10^{-8}$
11	1323	$1.3259 \times 10^{-7}$	$3.5551 \times 10^{-8}$	$9.7039 \times 10^{-8}$
14	1323	$6.5564 \times 10^{-8}$	$3.9317 \times 10^{-8}$	$2.6247 \times 10^{-8}$
16	1323	$4.6667 \times 10^{-8}$	$4.4355 \times 10^{-8}$	$2.3124 \times 10^{-9}$
17	1473	$1.7273 \times 10^{-6}$	$1.3937 \times 10^{-6}$	$3.3364 \times 10^{-7}$
18	1323	$1.5461 \times 10^{-7}$	$4.0254 \times 10^{-8}$	$1.1436 \times 10^{-7}$
20	1373	$2.5659 \times 10^{-7}$	$1.5270 \times 10^{-7}$	$1.0389 \times 10^{-7}$
21	1223	$7.2973 \times 10^{-9}$	$2.7986 \times 10^{-9}$	$4.4987 \times 10^{-9}$
22	1373	$2.7740 \times 10^{-7}$	$1.5581 \times 10^{-7}$	$1.2159 \times 10^{-7}$
24	1373	$2.1945 \times 10^{-7}$	$1.5131 \times 10^{-7}$	$6.8136 \times 10^{-8}$
25	1373	$2.0162 \times 10^{-7}$	$1.5093 \times 10^{-7}$	$5.0686 \times 10^{-8}$
26	1323	$5.8147 \times 10^{-8}$	$4.6512 \times 10^{-8}$	$1.1635 \times 10^{-8}$
27	1323	$4.5013 \times 10^{-8}$	$4.8863 \times 10^{-8}$	-----
31	1573	$1.0909 \times 10^{-5}$	$9.4380 \times 10^{-6}$	$1.4710 \times 10^{-6}$
32	1573	$6.4261 \times 10^{-6}$	$7.9601 \times 10^{-6}$	-----
33	1573	$1.2257 \times 10^{-5}$	$9.9063 \times 10^{-6}$	$2.3507 \times 10^{-6}$
47	1373	$2.6728 \times 10^{-7}$	$1.5078 \times 10^{-7}$	$1.1650 \times 10^{-7}$
55	1173	$1.9117 \times 10^{-9}$	$5.4201 \times 10^{-10}$	$1.3697 \times 10^{-9}$
58	1373	$3.0216 \times 10^{-7}$	$1.5080 \times 10^{-7}$	$1.5136 \times 10^{-7}$
60	1373	$2.3584 \times 10^{-7}$	$1.5154 \times 10^{-7}$	$8.4297 \times 10^{-8}$
76	1273	$1.7612 \times 10^{-8}$	$1.0793 \times 10^{-8}$	$6.8193 \times 10^{-9}$
78	1323	$3.2418 \times 10^{-8}$	$4.8613 \times 10^{-8}$	-----
79	1223	$7.9392 \times 10^{-9}$	$2.5323 \times 10^{-9}$	$5.4069 \times 10^{-9}$
85	1223	$8.0253 \times 10^{-10}$	$2.9516 \times 10^{-9}$	-----
88	1323	$5.6546 \times 10^{-8}$	$3.6332 \times 10^{-8}$	$2.0214 \times 10^{-8}$
90	1323	$6.8480 \times 10^{-8}$	$4.1331 \times 10^{-8}$	$2.7149 \times 10^{-8}$
91	1223	$8.4509 \times 10^{-9}$	$2.2686 \times 10^{-9}$	$6.1823 \times 10^{-9}$
94	826	$2.6869 \times 10^{-11}$	$3.4515 \times 10^{-17}$	$2.6869 \times 10^{-11}$

Table 4. Third law treatment for the reaction  $1/3 \text{U}_3\text{O}_8(\text{s}) + 1/6 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{UO}_2(\text{OH})_2(\text{g})$ .

run #	T (K)	$K_{\text{eq}}$	$-\Delta G^\circ$ (kJ/mol)	$-(\Delta G^\circ - \Delta H^\circ(298))/T$ (J/mol-K)	$\Delta H^\circ(298)$ (kJ/mol)
7	1323	-16.097	-177.10	41.019	231.38
8	1323	-16.043	-176.50	41.019	230.78
9	1323	-15.880	-174.70	41.019	228.98
11	1323	-15.668	-172.37	41.019	226.65
14	1323	-15.713	-172.87	41.019	227.15
16	1323	-19.135	-210.52	41.019	264.80
rejected					
17	1473	-14.198	-173.92	39.601	232.26
18	1323	-15.459	-170.08	41.019	224.36
20	1373	-15.347	-175.22	40.535	230.88
21	1223	-18.268	-185.79	42.029	237.20
22	1373	-15.097	-172.37	40.535	228.03
24	1373	-15.802	-180.42	40.535	236.08
25	1373	-16.107	-183.90	40.535	239.56
26	1323	-17.233	-189.59	41.019	243.87
31	1573	-12.739	-166.63	38.707	227.52
33	1573	-12.037	-157.45	38.707	218.34
47	1373	-15.278	-174.43	40.535	230.10
55	1173	-19.725	-192.41	42.557	242.34
58	1373	-15.016	-171.44	40.535	227.10
60	1373	-15.584	-177.93	40.535	233.59
76	1273	-18.244	-193.13	41.516	245.99
79	1223	-18.463	-187.78	42.029	239.19
88	1323	-17.238	-189.65	41.019	243.93
90	1323	-16.862	-185.51	41.019	239.79
91	1223	-18.421	-187.35	42.029	238.76
94	826	-23.660	-162.49	46.533	200.93 rejected
					$233.49 \pm 7.12$

$\Delta H_f^\circ(298)$   
(kJ/mol)

$\text{U}_3\text{O}_8(\text{s})$	$-3574.80 \pm 2.50$
$\text{H}_2\text{O}(\text{g})$	$-241.83 \pm 0.04$
$\text{UO}_2(\text{OH})_2(\text{g})$	$-1199.94 \pm 10.25$

Table 5. Summary of transpiration experiments on uranium oxide in the presence of oxygen and chlorine.

run #	T (K)	time (min)	moles total	p(O <sub>2</sub> ) (atm)	p(Cl <sub>2</sub> ) (atm)	p(U total) (atm)
1	1174.6	110.5	0.10239	1.696x10 <sup>-4</sup>	1.000	5.0878x10 <sup>-4</sup>
2	1174.8	89.0	0.08251	0.5014	0.4986	1.8839x10 <sup>-4</sup>
3	1173.5	100.0	0.09266	0.7496	0.2504	8.4785x10 <sup>-5</sup>
4	1174.7	106.0	0.08593	0.1431	0.8569	2.6841x10 <sup>-4</sup>
5	1174.6	99.0	0.09183	0.5007	0.4993	1.2398x10 <sup>-4</sup>
6	1174.5	98.0	0.09086	0.2502	0.7498	1.9928x10 <sup>-4</sup>
7	1174.8	82.0	0.07599	0.8767	0.1233	4.2017x10 <sup>-5</sup>
8	1175.1	104.0	0.09628	2.454x10 <sup>-4</sup>	1.000	7.3612x10 <sup>-4</sup>



Table 6. Third law treatment for the reaction  $1/3 \text{U}_3\text{O}_8(\text{s}) + \text{Cl}_2(\text{g}) = \text{UO}_2\text{Cl}_2(\text{g}) + 1/3 \text{O}_2(\text{g})$ .

run #	T (K)	$K_{\text{eq}}$	$-\Delta G^\circ$ (kJ/mol)	$-(\Delta G^\circ - \Delta H^\circ(298))/T$ (J/mol-K)	$\Delta H^\circ(298)$ (kJ/mol)
—					
1	1174.6	$2.816 \times 10^{-5}$	-102.33	91.873	210.24 rejected
2	1174.8	$3.002 \times 10^{-4}$	-79.23	91.872	187.16
3	1173.5	$3.076 \times 10^{-4}$	-78.82	91.895	186.74
4	1174.7	$1.638 \times 10^{-4}$	-85.13	91.872	193.05
5	1174.6	$1.972 \times 10^{-4}$	-83.32	91.873	191.23
6	1174.5	$1.675 \times 10^{-4}$	-84.91	91.874	192.81
7	1174.8	$3.262 \times 10^{-4}$	-78.41	91.872	186.34
8	1175.1	$4.608 \times 10^{-5}$	-97.55	91.862	<u>205.50 rejected</u> 189.56 $\pm$ 3.15
		$\Delta H_f^\circ(298)$ (kJ/mol)			
$\text{U}_3\text{O}_8(\text{s})$		<u><math>-3574.80 \pm 2.50</math></u>			
$\text{UO}_2\text{Cl}_2(\text{g})$		$-1002.04 \pm 3.26$			

Table 7. Summary of best assessed  $\Delta H_f^\circ(298)$  values for uranium vapor species.

species	$\Delta H_f^\circ(298)$ (kJ/mol)
UO <sub>3</sub> (g)	-796.74 ± 3.52
UO <sub>2</sub> F <sub>2</sub> (g)	-1369.22 ± 2.87
UO <sub>2</sub> Cl <sub>2</sub> (g)	-999.64 ± 2.40
UO <sub>2</sub> (OH) <sub>2</sub> (g)	-1199.94 ± 10.25
UO <sub>2</sub> FOH(g)	-1284.58 estimate
UO <sub>2</sub> ClOH(g)	-1099.79 estimate
UO <sub>2</sub> FCI(g)	-1184.43 estimate

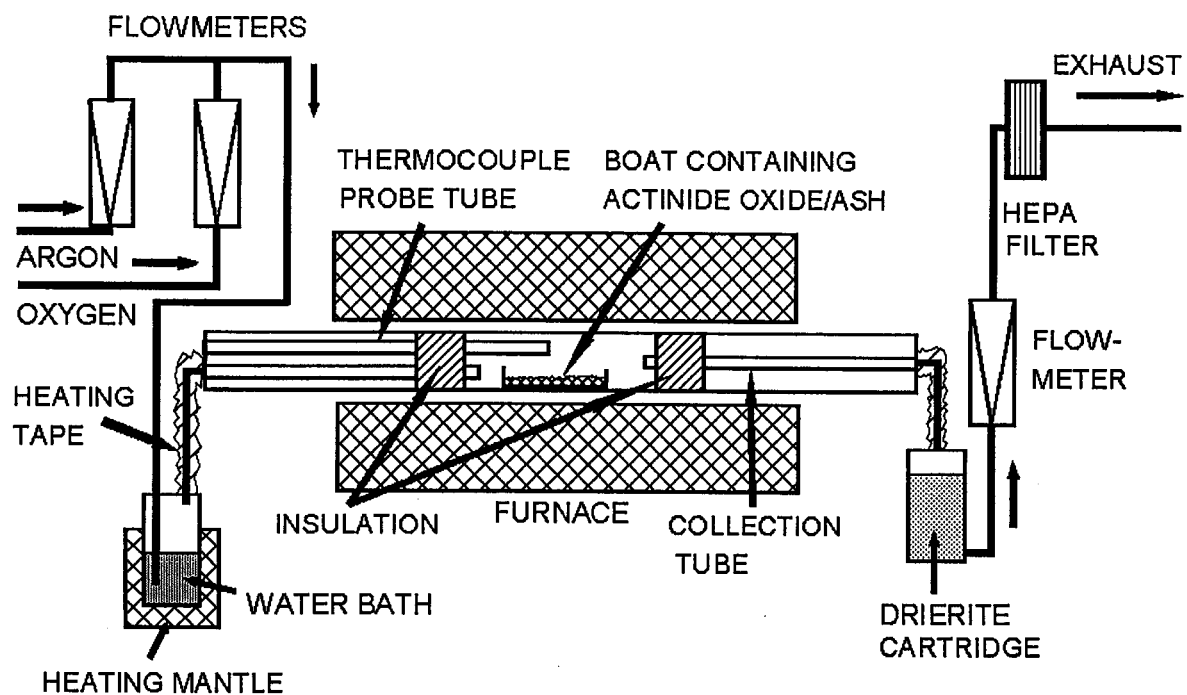


Figure 1. Schematic of the transpiration apparatus used for the  $\text{U}_3\text{O}_8(\text{s})$  transpiration experiments in the presence of  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ .

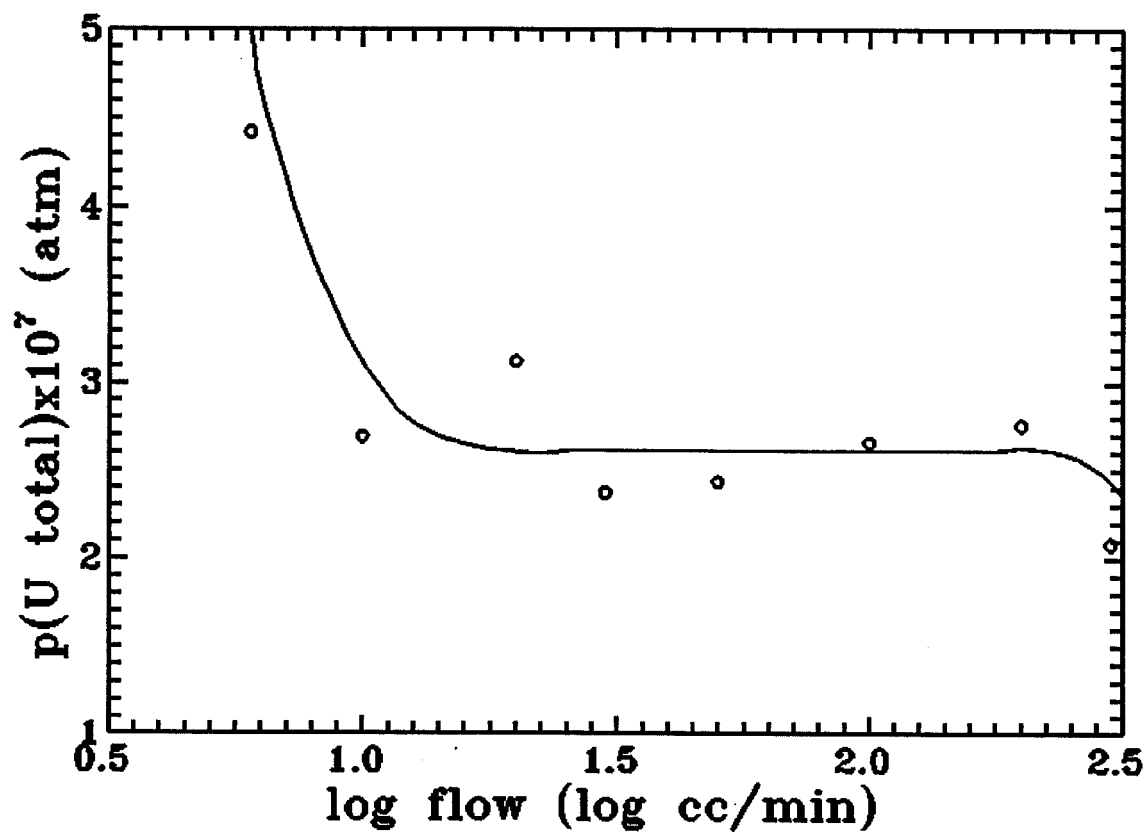


Figure 2. Plot of  $O_2(g)$  flow rate in the furnace tube versus apparent total pressure of uranium where  $T = 1373\text{ K}$ ,  $p(O_2) = 0.4\text{ atm}$  and  $p(H_2O) = 0.6\text{ atm}$ . A plateau region is present from about 25 to  $500\text{ cm}^3/\text{min}$ .

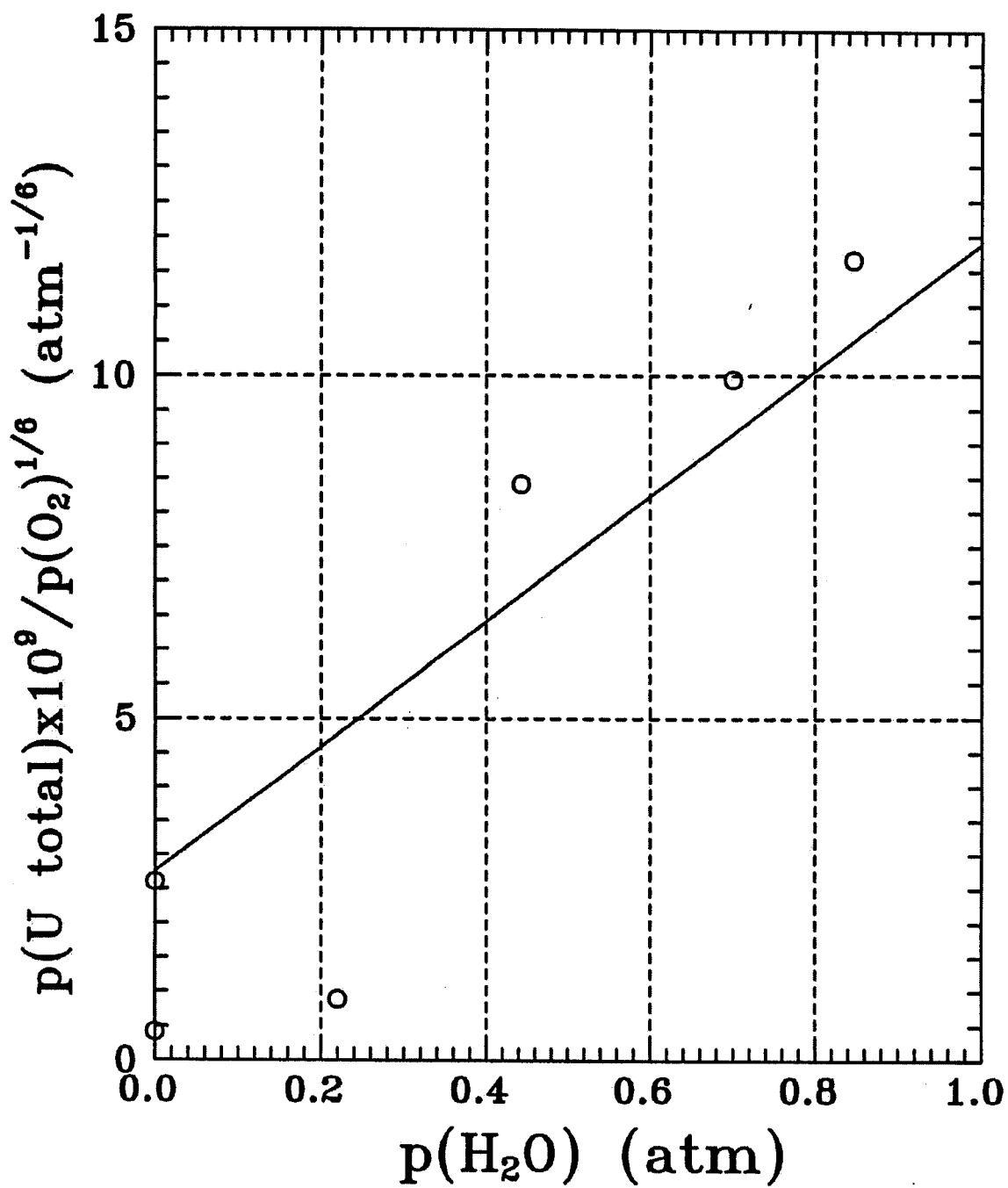


Figure 3. Plot of  $p(\text{U total})/p(\text{O}_2)^{1/6}$  versus  $p(\text{H}_2\text{O})$  at 1223 K. The plot increases linearly with water vapor pressure which indicates that  $\text{UO}_2(\text{OH})_2(\text{g})$  is formed in the vapor.

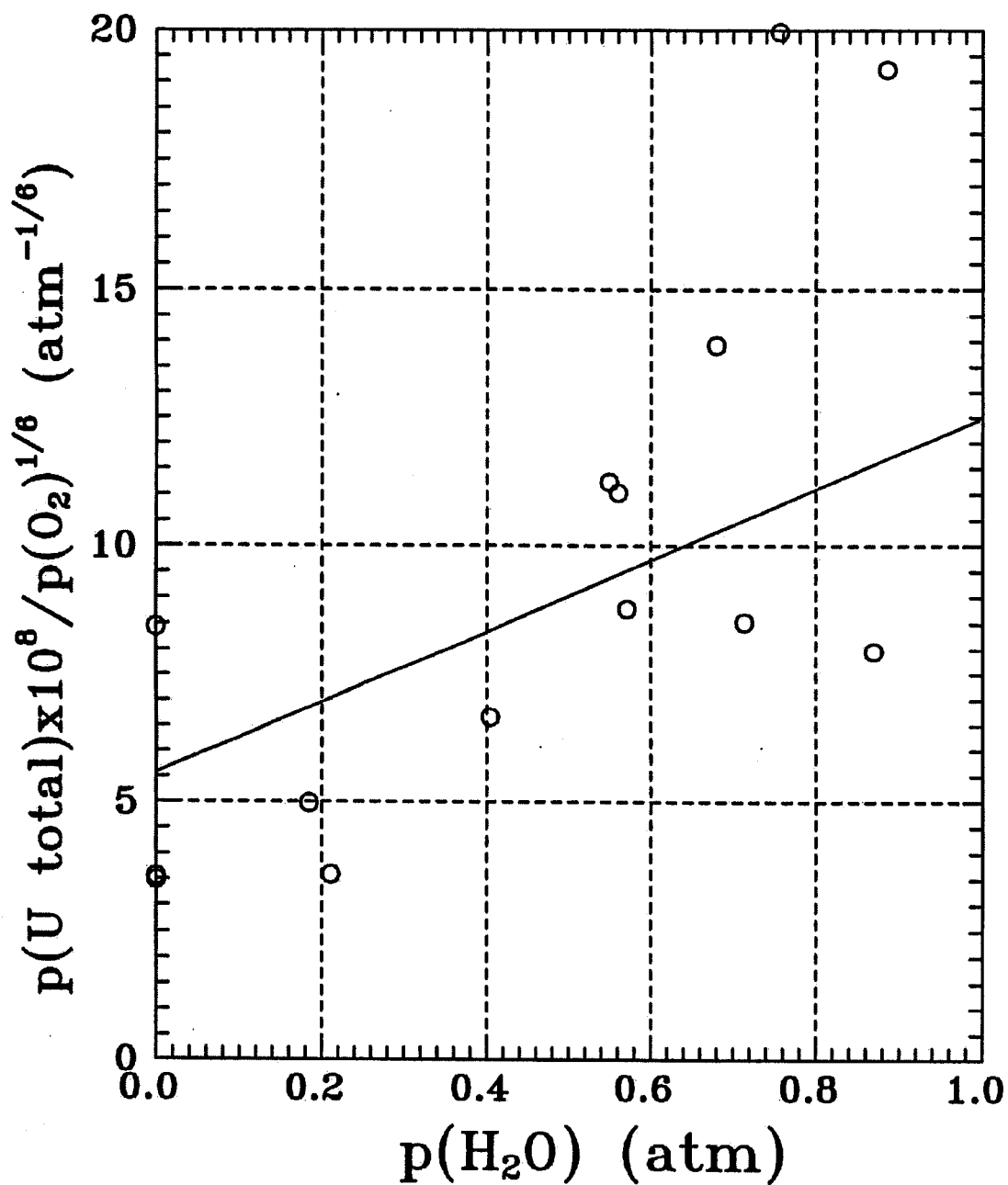


Figure 4. Plot of  $p(\text{U total})/p(\text{O}_2)^{1/6}$  versus  $p(\text{H}_2\text{O})$  at 1323 K. Although there is a lot of scatter in the data, the curve seems to increase linearly with water vapor pressure which indicates the presence of  $\text{UO}_2(\text{OH})_2(\text{g})$ .

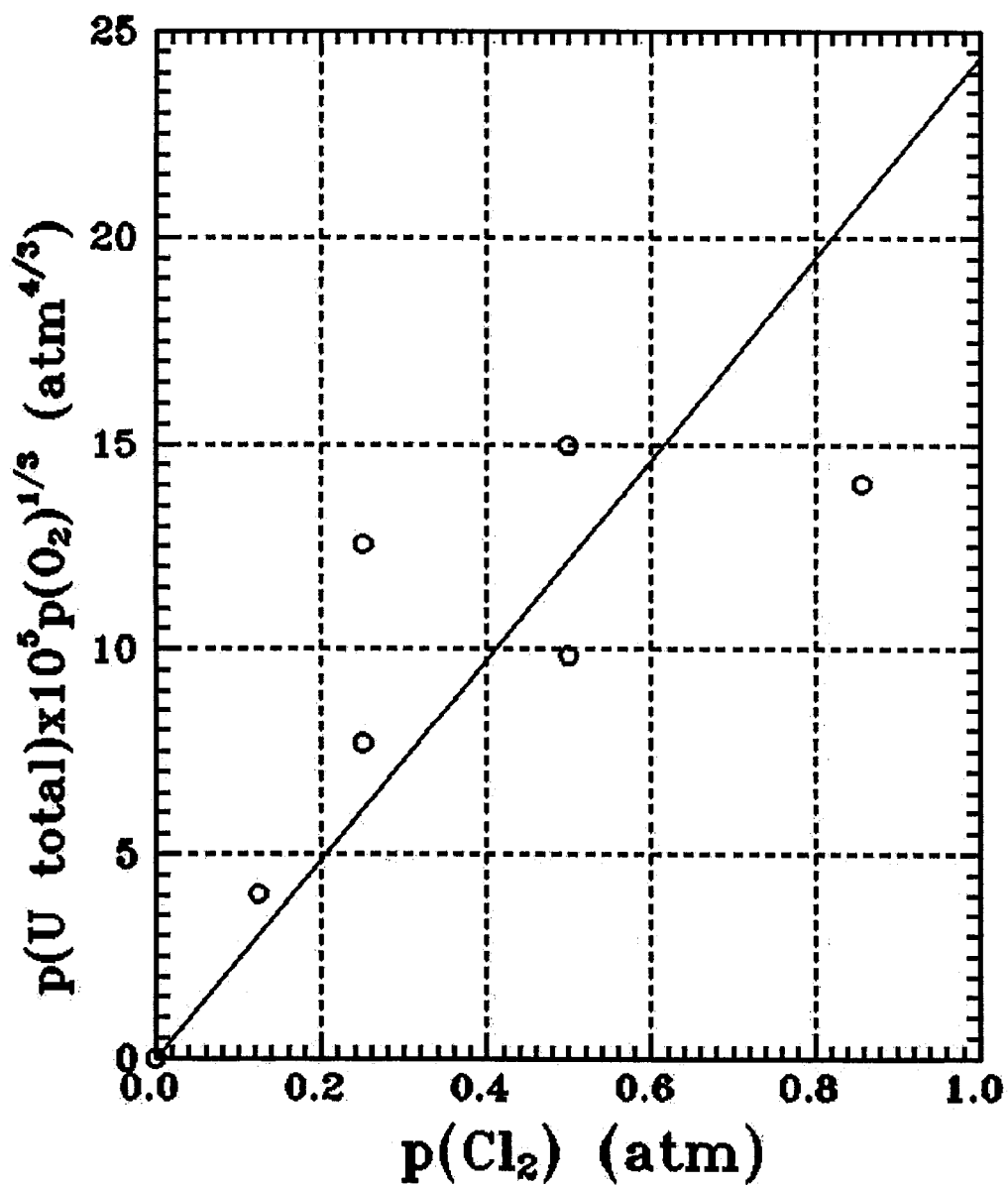


Figure 5. Plot of  $p(\text{U total})p(\text{O}_2)^{1/3}$  versus  $p(\text{Cl}_2)$  at 1175 K. The plot increases linearly with chlorine pressure indicating that  $\text{UO}_2\text{Cl}_2(\text{g})$  is formed in the vapor.

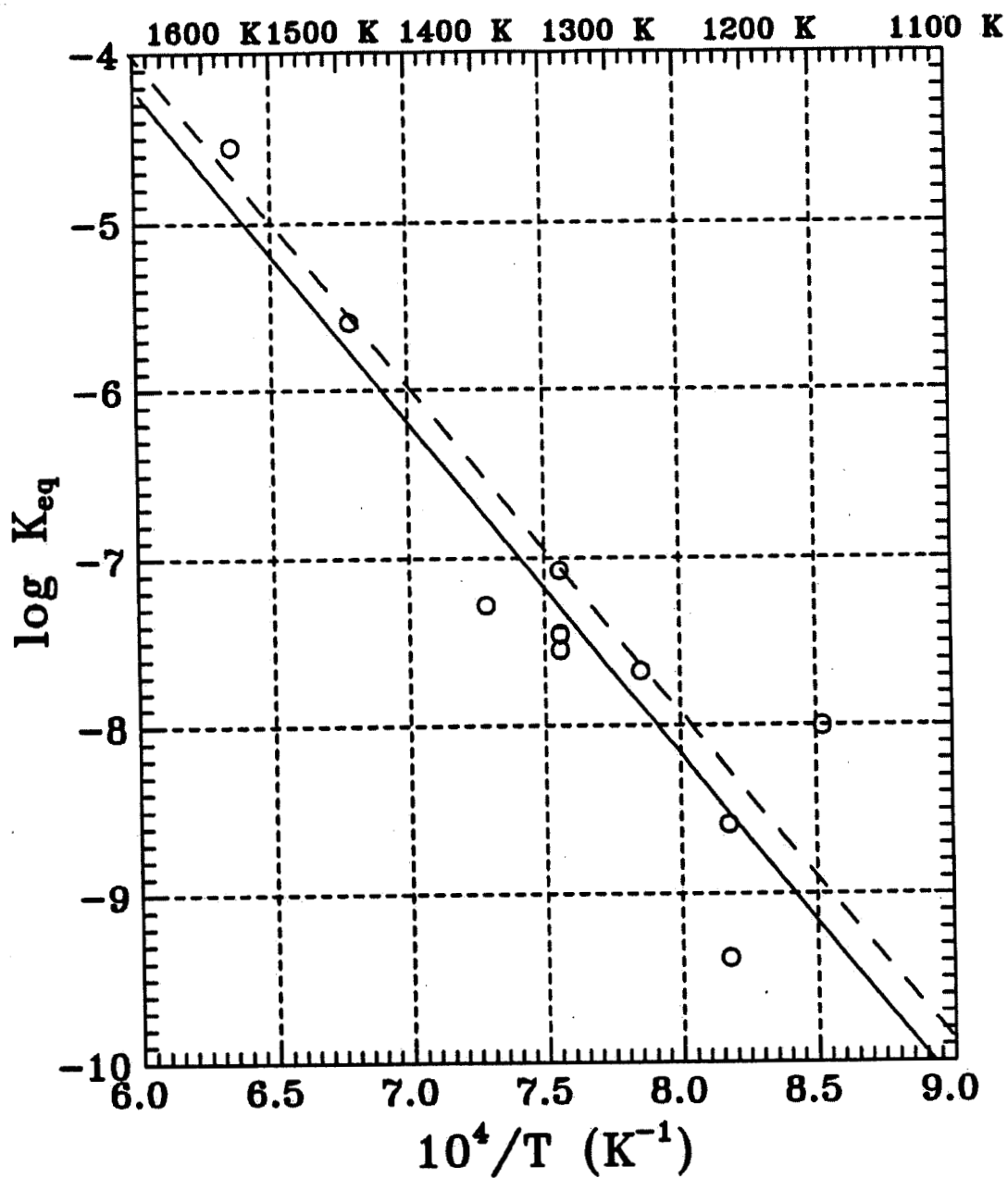


Figure 6. Plot of  $\log p(\text{UO}_3)$  versus  $10^4/T$ . The solid line is the third law fit of the data and the dashed line is the data of Dharwadkar, *et al.* [2] and Ackermann, *et al.* [1] treated by the third law method and averaged.



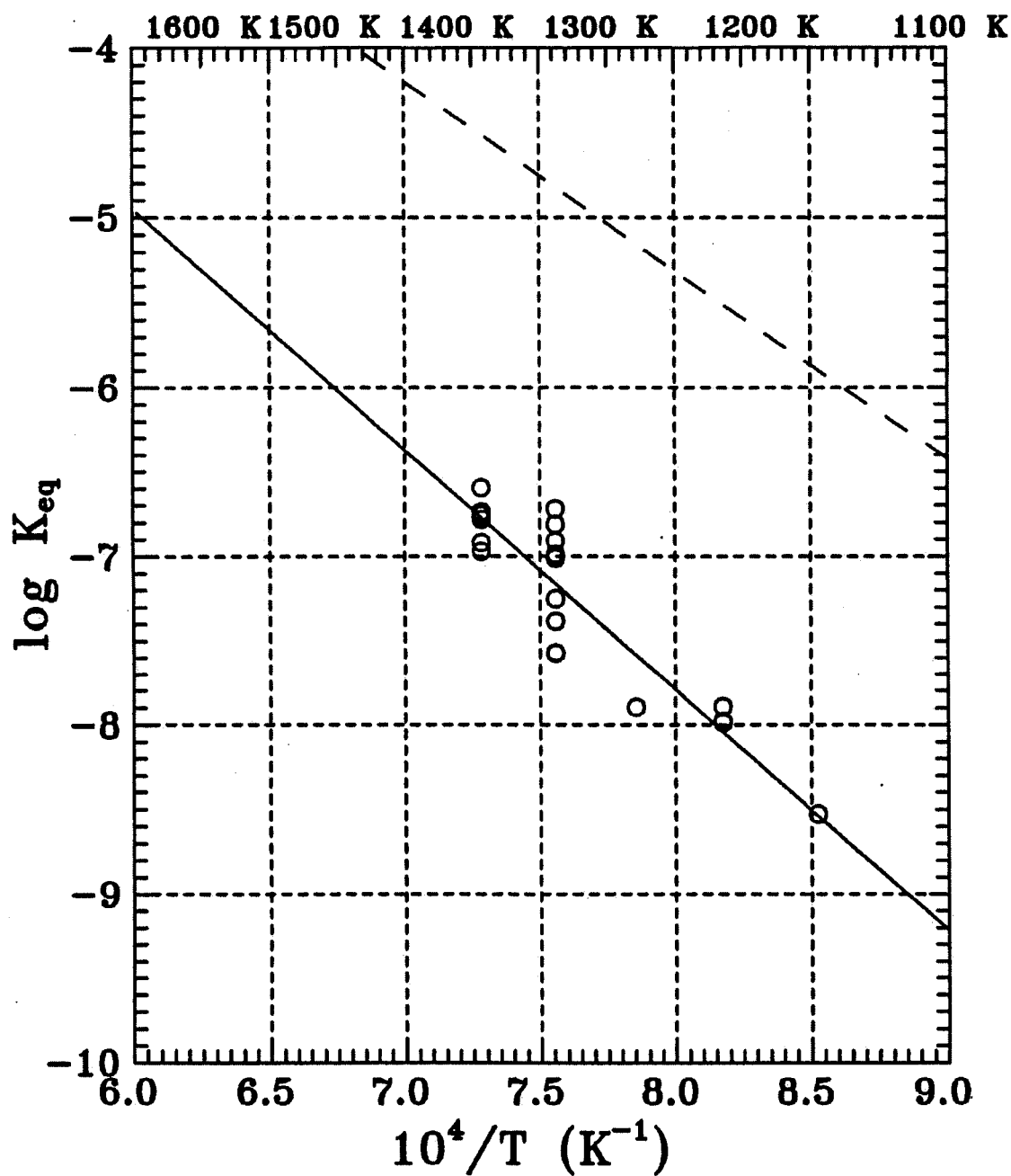


Figure 7. Plot of  $\log p(\text{UO}_2(\text{OH})_2)$  versus  $10^4/T$ . The solid line is the third law fit of the data and the dashed line is the data of Dharwadkar, *et al.* [2] treated by the third law method.

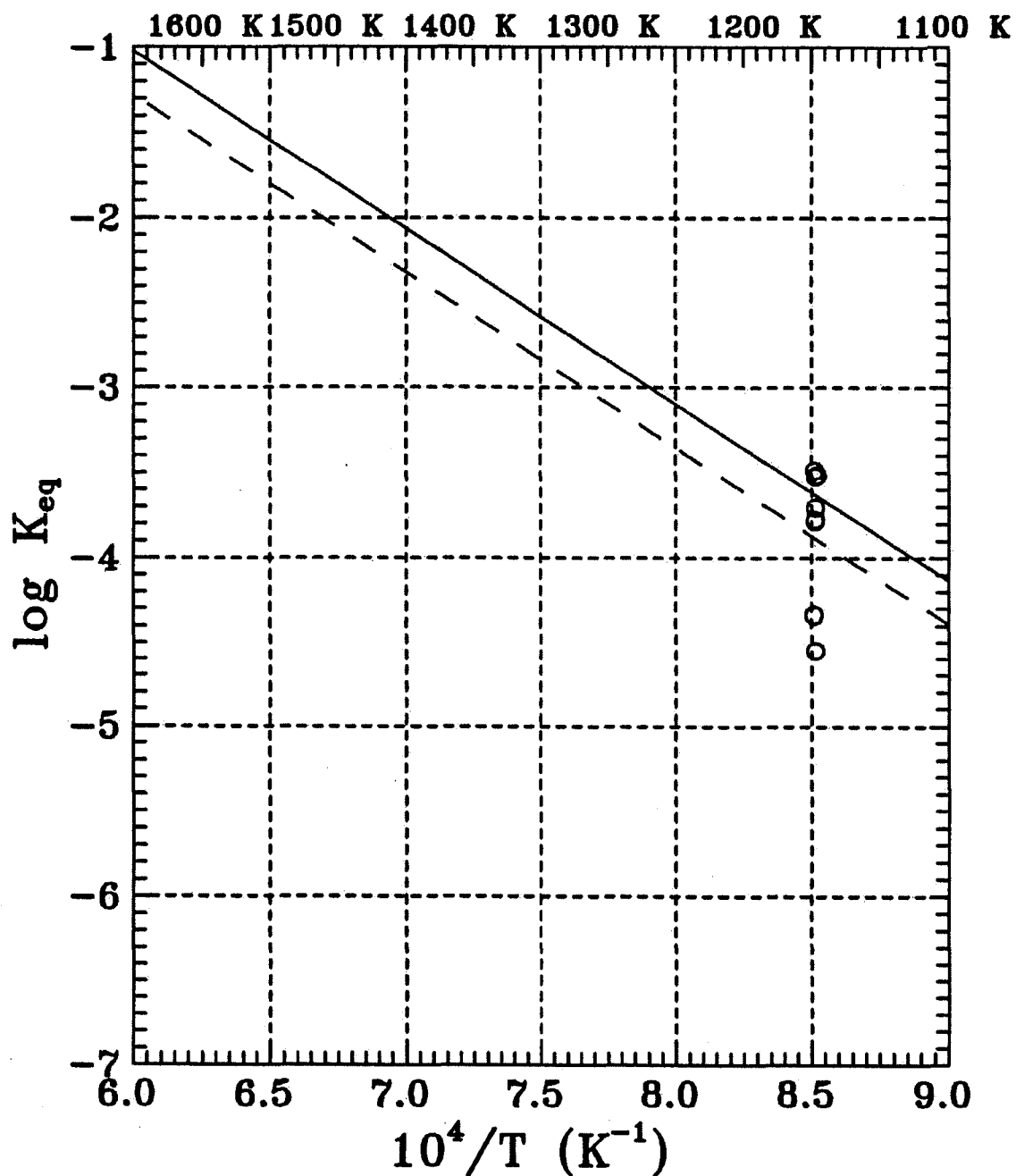


Figure 8. Plot of  $\log p(\text{UO}_2\text{Cl}_2)$  versus  $10^4/T$ . The solid line is the third law fit of the data and the dashed line is the data of Cordfunke and Prins [3] treated by the third law method.

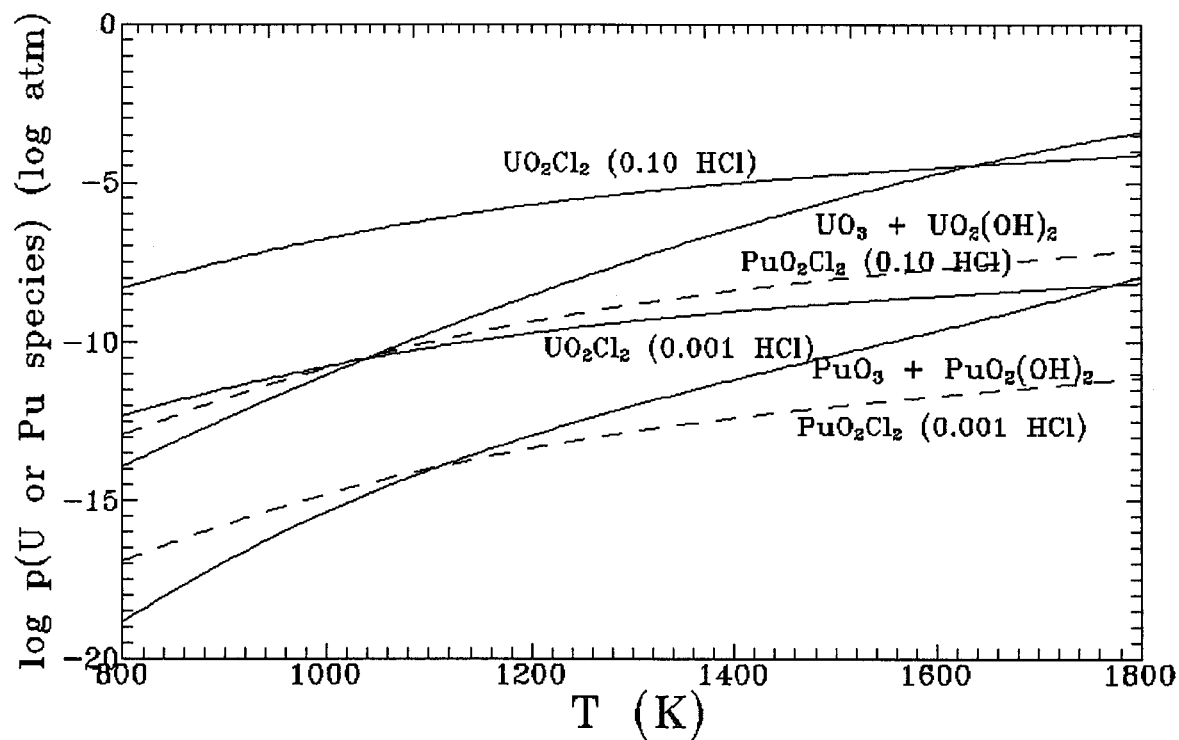


Figure 9. Plot of  $\log p(\text{AnO}_3)$ ,  $\log p(\text{AnO}_2(\text{OH})_2)$ , and  $\log p(\text{AnO}_2\text{Cl}_2)$  ( $\text{An} = \text{U}$  or  $\text{Pu}$ ) versus  $T$  where  $p(\text{O}_2) = 0.10$  atm,  $p(\text{H}_2\text{O}) = 0.10$  atm,  $p(\text{HCl}) = 0.10$  or  $0.001$  atm. The species,  $\text{AnO}_2\text{ClOH(g)}$ , is not shown here but would also be expected to be important.

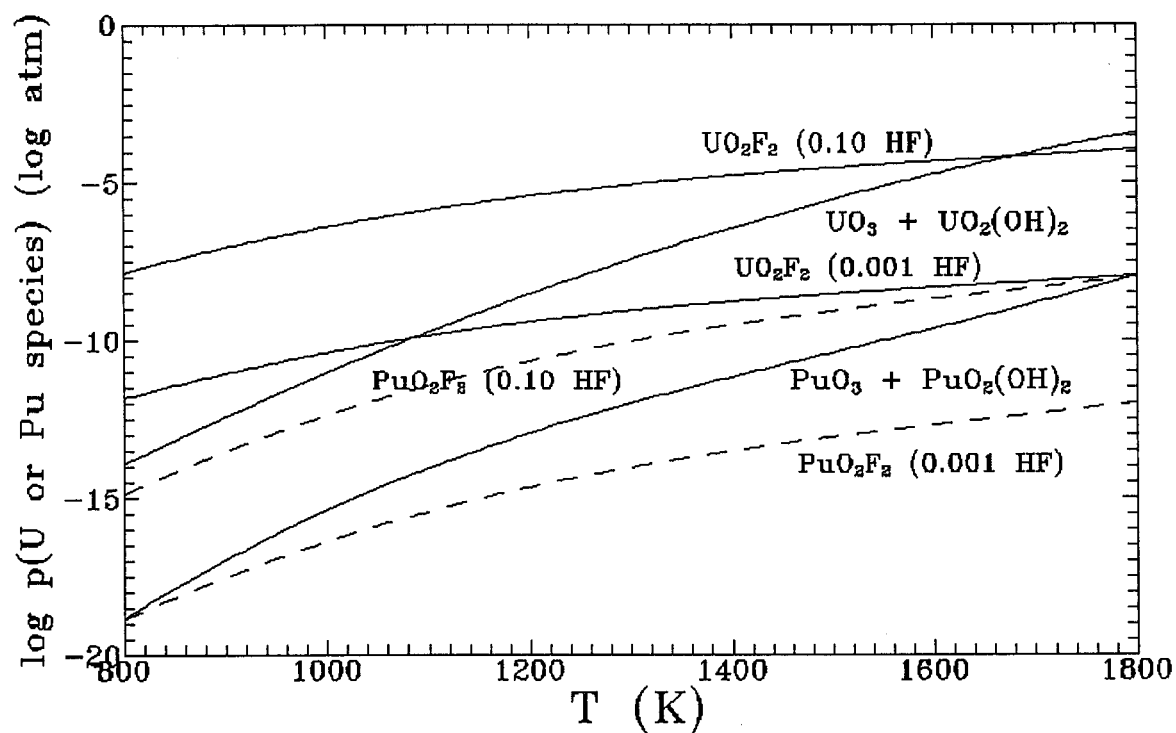


Figure 10. Plot of  $\log p(\text{AnO}_3)$ ,  $\log p(\text{AnO}_2(\text{OH})_2)$ , and  $\log p(\text{AnO}_2\text{F}_2)$  (An= U or Pu) versus T where  $p(\text{O}_2) = 0.10$  atm,  $p(\text{H}_2\text{O}) = 0.10$  atm, and  $p(\text{HF}) = 0.10$  or  $0.001$  atm. The species,  $\text{AnO}_2\text{FOH}(\text{g})$ , is not shown here but would also be expected to be important.